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Atomistic Simulations of the Physical Properties of Nitrate Esters

by Steven W. Bunte and Martin S. Miller

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Atomistic Simulations of the Physical Properties of Nitrate Esters

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Abstract

Atomistic simulations have advanced to the degree that the material properties of actual Army gun propellants can be predicted *a priori*. For example, we have used the COMPASS force field to predict the density of the gun propellant JA2 and its energetic ingredients. The predicted density of the propellant is within 1.6% of its measured value. These results are the first *a priori* prediction of the density of an Army gun propellant and clearly suggest that this methodology can be a valuable tool in the design of new high energy propellant formulations for use in the Future Combat System.

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1. Introduction

Research in Army gun propulsion is currently being driven by the requirements of The Army's Transformation Strategy. This transformation, which is targeted to be complete in the 2010 timeframe, will result in an Objective Force that is more deployable, lethal, survivable, and sustainable than the present force. In terms of gun propulsion, attainment of this vision will require new propellant formulations that contain more energy and are less sensitive than the propellants currently fielded. This report presents the first application of atomistic modeling to compute the macroscopic properties of real, multi-ingredient gun propellants. This new technology, which represents the fruition of decades of research, may well prove vital to meeting the ambitious performance and timeline goals set for the Future Combat System.

In the past, the determination of gun propellant properties has necessitated direct measurement. This would require the formulation of a large number of candidate mixes. The property of interest would be measured; those that exhibited promise would be kept for further testing, and those that were less than promising were discarded. This process is both inefficient and expensive. In addition, the formulation process can result in significant hazardous waste streams that can be costly to remediate. The availability of atomistic and molecular modeling strategies capable of predicting material properties such as density, stability, mechanical properties, and ingredient compatibility would revolutionize the design and formulation of new gun propellants. This report demonstrates that such a valuable tool is now becoming available for practical use. Although computer speed has increased dramatically in recent years, the modeling of large molecular systems and condensed phases has been prohibitive from a first-principles approach. A more empirical approach based on atomic force fields, however, has proved most promising. In less complex cases where both may be employed, the force field method is several orders of magnitude faster than any *ab initio* method. In addition, the most important interaction terms in simulating the condensed phase are the nonbonding forces (in particular, the dispersion forces), which are extremely difficult to accurately describe using *ab initio* methods. Papers have recently appeared in the literature which document the accurate prediction of a wide variety of properties of both molecules in the condensed phase and in isolation (gas phase) using the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, Molecular Simulations, Inc.) force field (Sun 1998). The COMPASS force field has been specifically designed for material science applications. It is a class II force field in that it employs complex functional forms and is derived from extensive *ab initio* data. Consequently, it can be used

to accurately predict several molecular properties, including molecular structures, conformations, and vibrations. The nonbonded parameters in COMPASS have been optimized using condensed-phase (liquid and crystal) data so that several thermophysical properties of molecular liquids and crystals can be well reproduced. COMPASS has been parameterized to study the most common organic molecules, organic and inorganic polymers, zeolites, and metal/transition-metal oxides. However, some of the functional groups required to model energetic materials have not (until recently) been parameterized and included in the COMPASS force field (Bunte and Sun 2000). For instance, the gun propellant JA2 is composed of three principal energetic ingredients: nitrocellulose (NC, $C_6H_{7.55}N_{2.45}O_{9.90}$), nitroglycerin (NG, $O_2NOCH_2-CHONO_2-CH_2ONO_2$), and diethyleneglycol dinitrate (DEGDN, $O_2NO-(CH_2)_2-O-(CH_2)_2-ONO_2$). In the propellant blend, the NC is present as an energetic binder, and both NG and DEGDN serve as an energetic plasticizing agent. The common chemical feature in each of these compounds is the nitrate ester (-ONO₂) functional group. Nitro (-NO₂) containing compounds have been parameterized in the COMPASS force field and contain most, but not all, of the parameters needed to model the nitrate esters. Using methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, and butyl nitrate as model compounds, we recently completed the parameterization and validation of the additional atom types needed to model the nitrate ester functional group (Bunte and Sun 2000). Room temperature molecular dynamics simulations of the densities of these model compounds varied from experiment by an average of 0.8%. Having successfully modeled the densities of these simple nitrates, we had the confidence to attempt to simulate the densities of NG, DEGDN, NC, and JA2. This report presents the *a priori* prediction of the densities of NG, DEGDN, NC, and JA2 using the COMPASS force field.

2. The Model

2.1 The COMPASS Force Field

The functional forms used in the COMPASS force field are the same as the CFF-type force field (Sun 1998).

$$\begin{aligned}
E_{total} = & \sum_b \left[k_2 (b - b_o)^2 + k_3 (b - b_o)^3 + k_4 (b - b_o)^4 \right] \\
& + \sum_\theta \left[k_2 (\theta - \theta_o)^2 + k_3 (\theta - \theta_o)^3 + k_4 (\theta - \theta_o)^4 \right] \\
& + \sum_\phi \left[k_1 (1 - \cos \phi) + k_2 (1 - \cos 2\phi) + k_3 (1 - \cos 3\phi) \right] \\
& + \sum_\chi k_2 (\chi - \chi_o)^2 \\
& + \sum_{b,b'} k (b - b_o) (b' - b'_o) \\
& + \sum_{b,\theta} k (b - b_o) (\theta - \theta_o) \\
& + \sum_{b,\phi} (b - b_o) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] \\
& + \sum_{\theta,\phi} (\theta - \theta_o) [k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] \\
& + \sum_{b,\theta} k (\theta' - \theta'_o) (\theta - \theta_o) \\
& + \sum_{\theta,\theta,\phi} k (\theta - \theta_o) (\theta' - \theta'_o) (\phi - \phi_o) \\
& + \sum_{i,j} \frac{q_i q_j}{r_{ij}} \\
& + \sum_{i,j} \epsilon_{ij} \left[2 \left(\frac{r_{ij}^o}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^o}{r_{ij}} \right)^6 \right].
\end{aligned}
\tag{1}$$

The potential functions can be divided into two categories—valence terms, including the diagonal and off-diagonal cross coupling terms, and the nonbonded interaction terms. The valence terms include E_b , E_θ , E_ϕ , and E_χ for bond, angle, torsion, and out-of-plane angle coordinates, respectively, and $E_{bb'}$, $E_{b\theta}$, $E_{b\phi}$, $E_{\theta\theta'}$, and $E_{\theta\theta'\phi}$ for the cross-coupling terms between internal coordinates. The cross-coupling terms are important for predicting vibrational frequencies and structural variations associated with conformational changes. Among the cross-coupling terms, the bond-bond $E_{bb'}$, bond-angle $E_{b\theta}$, and bond-torsion $E_{b\phi}$, are the most significant.

The nonbonded terms, which include a “soft” Lennard-Jones 9-6 (L-J) potential for the van der Waals (vdW) interaction and a Coulombic term for the electrostatic interactions, are used for interactions between pairs of atoms that are separated by three or more intervening atoms, or those that belong to different molecules. The L-J parameters (ϵ and r^o) for like atom pairs are adjustable parameters. For unlike atom pairs, a sixth order combination law (Sun 1998) is used to calculate the off-diagonal parameters as follows.

$$r_{i,j}^o = \left[\frac{(r_i^o)^6 + (r_j^o)^6}{2} \right]^{\frac{1}{6}}. \quad (2)$$

$$\varepsilon_{i,j} = 2\sqrt{\varepsilon_i \cdot \varepsilon_j} \left[\frac{(r_i^o)^3 \cdot (r_j^o)^3}{(r_i^o)^6 + (r_j^o)^6} \right]. \quad (3)$$

The electrostatic interaction is represented by the partial atomic charge model using charge bond-increments, δ_{ij} , as a measure of the charge separation between two valence-bonded atoms. The net partial charge of an atom, q_i , is obtained as a summation of all charge bond-increments related to this atom:

$$q_i = \sum_j \delta_{ij}. \quad (4)$$

The details on the methodology of parameterization are reported elsewhere (Sun 1998). Basically, the valence parameters (both diagonal and off-diagonal cross-coupling terms) and charge bond increments were derived by least-squares fitting to the HF/6-31g(d) data calculated for the model compounds, methyl and ethyl nitrate. The *ab initio* data includes electrostatic potentials, energies, and the first and second derivatives of the energies. The resulting parameters were subsequently scaled by a set of generic factors to correct the systematic errors of the HF/6-31g(d) calculations. The resulting force field (quantum mechanics force field or QMFF) was then systematically validated and modified to fit experimental or higher-level *ab initio* data for molecules in isolation. The vdW nonbonded parameters (L-J 9-6 terms) were initially transferred from other organic systems (Sun 1998). After the valence parameters were derived, they were then subject to optimization using molecular dynamics (MD) simulations of liquids. The whole validation and optimization procedure was repeated until a consistent fit was obtained for both the gaseous and condensed phases.

2.2 Molecular Dynamics Simulations

MD simulations were carried out using the software package InsightII/Discovery. For liquids and crystals, a periodic cell with explicit minimum image convention (Frenkel and Smit 1996; Allen and Tildesley 1987) was built for each of the compounds studied. The cubic cell edges ranged from 20-30 Å in length and contained 1000-1500 atoms. A charge group-based cutoff method with tail correction was used to evaluate the nonbonded interactions in all of the liquid simulations. It is assumed in the charge group-based cutoff method that the radial distribution functions converged to unity beyond the cutoff distance (Frenkel and Smit 1996; Allen and Tildesley 1987), which in our simulations was 9.5 Å. For the crystal simulations, the Ewald summation method (Frenkel and Smit 1996; Allen and Tildesley 1987) was used for both the vdW and the electrostatic terms. Constant pressure and temperature (NPT) simulations were carried out using a modified velocity Verlet (Frenkel and Smit

1996; Allen and Tildesley 1987) integrator with the Berendsen (Berendsen et al. 1984) pressure control method for the validation calculations. A time step of 1 fs was used in all of the MD simulations. The initial configuration of the material being simulated was constructed using the following procedure. First, molecules were uniformly placed into a cubic cell that was large enough so that there was no strong repulsion between any two molecules. The system was then randomized by running a constant volume and temperature (NVT) simulation for several hundred steps at a temperature of 2000 K, which is well over the boiling point of all the liquids studied. Following randomization, the system was gradually compressed to the target density in a high pressure (5,000–50,000 bar) constant pressure and temperature (NPT) simulation. Finally, a pre-equilibrium process was performed using a simulated annealing technique, during which the temperature was gradually reduced from 2000 K to 300 K. The pre-equilibration took about 50–100 ps, which is usually adequate for liquids of small molecules (Sun 1998). The average periods were 50 ps for NVT simulations and 100 ps for NPT simulations. For each simulation run, 10 configurations were constructed. Each configuration consisted of a random arrangement of the molecules within the simulation cell. These configurations were then allowed to relax under the influence of the COMPASS force field, and the density of each configuration was computed. The simulated densities presented here are an average of the 10 configuration densities.

3. Results

3.1 Gas Phase Molecular Properties

The validation of molecular properties for molecules in the gas phase was based on the molecular mechanics calculations. These calculations were performed on the isolated (i.e., gas phase) molecules of DEGDN and NG. In each case, the calculations consisted of full energy minimizations followed by calculation of the Hessian matrix. Because of the lack of experimental data, these results were compared with the results from high level *ab initio* calculations.

3.1.1 Structures

The most basic property to predict is the structure of the molecule. For example, it is well known that a small deviation in the bond length can have a potentially significant effect on the liquid or crystal density obtained from an MD simulation. Consequently, it is extremely important to make sure that the structural properties are accurately modeled using the force field prior to running the condensed phase simulations. A graph of the force field calculated bond lengths and bond angles of DEGDN and NG are plotted vs. the B3LYP/6-311g(d,p) results in Figures 1 and 2, respectively.

Comparison of DEGDN and NG Bond Lengths

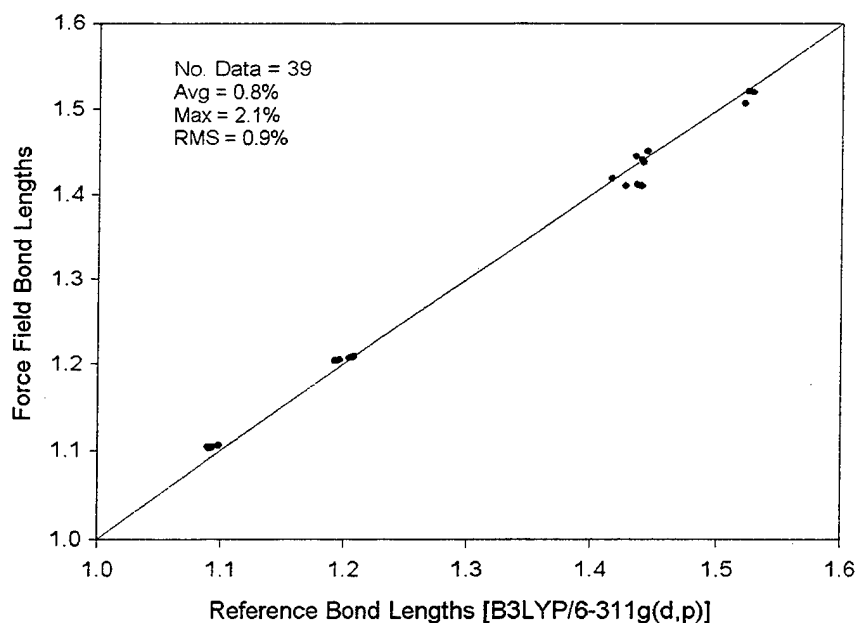


Figure 1. Comparison of the bond lengths (\AA) of NG and DEGDN calculated using the force field and the B3LYP/6-311g(d,p) reference.

Comparison of DEGDN and NG Bond Angles

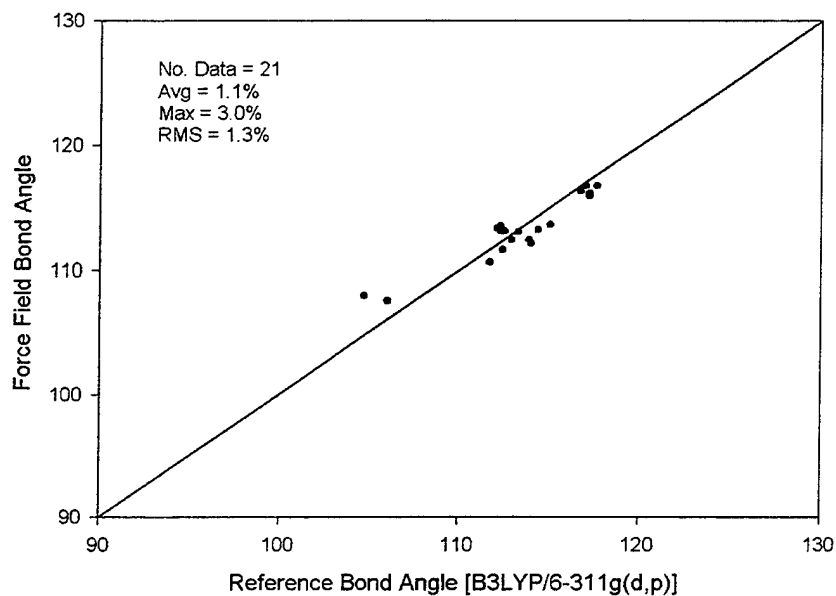


Figure 2. Comparison of the bond lengths (in degrees) of NG and DEGDN calculated using the force field and the B3LYP/6-311g(d,p) reference.

There are a total of 39 data points for the bond lengths and 21 for the bond angles. As indicated in the figures, excellent agreement between the calculated (force field) and reference (B3LYP) data is obtained. The average percentage deviation in the bond lengths is 0.8%, and the maximum percentage deviation is 2.1%. The root mean squares (RMS) percentage deviation is 0.9%. For the bond angles, the average percentage deviation is 1.1%, with a maximum percentage deviation of 3.0%. The RMS percentage deviation is 1.3%. These results are consistent with the results obtained on other molecules using the COMPASS force field (Sun 1998).

3.1.2 Vibrational Frequencies

A molecular mechanics (MM) force field is different from a spectroscopic force field. Generally speaking, by simultaneously fitting various properties including structures, conformations, and vibrational frequencies, a MM force field can only predict the vibrational frequencies with a modest level of accuracy (an RMS deviation of approximately 20-50 cm^{-1}). Frequency predictions obtained by COMPASS generally fall into this category. Again, as a result of the lack of experimental data on NG and DEGDN, the comparison was performed between the force field and B3LYP/6-311g(d,p) results. In Figure 3, the COMPASS frequencies are plotted against the B3LYP frequencies.

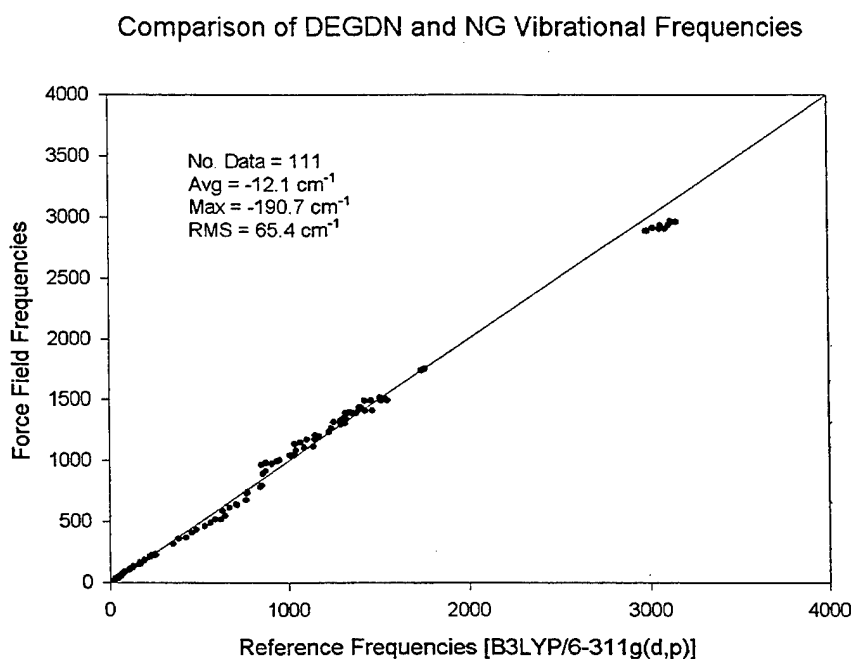


Figure 3. Comparison of the vibrational frequencies (in cm^{-1}) of NG and DEGDN calculated using the force field and the B3LYP/6-311g(d,p) reference.

There are 111 data points plotted with an average deviation of -12.1 cm^{-1} . The maximum absolute deviation is -190.7 cm^{-1} , and the RMS deviation is 65.4 cm^{-1} . The largest deviations are found in the high frequency region ($>3000\text{ cm}^{-1}$), which correspond to the C-H stretch modes.

3.2 Condensed Phase Molecular Properties

Constant pressure and temperature (NPT) MD simulations, as described previously, were performed to calculate the densities of NG and DEGDN. Both of these materials are liquids at room temperature; hence, of the materials studied, these simulations are the least complicated of the four. The measured density of NG is 1.5910 g/cm^3 (Federoff and Sheffield 1972); the simulation predicted a value of 1.6232 g/cm^3 , a difference of 2%. For DEGDN, the experimental density is 1.3770 g/cm^3 (Dean 1973), and the predicted density is 1.3785 g/cm^3 , a difference of 0.1%. The agreement obtained for these materials is consistent with that observed in many other molecules that COMPASS covers.

3.2.1 Nitrocellulose (NC) as an Ingredient

NC represents a considerably more difficult case than NG and DEGDN. Present in all conventional gun propellants, NC is a long-chain polymer which has three possible sites of nitration, located at C2, C3, and C6 on each monomer unit as shown in Figure 4.

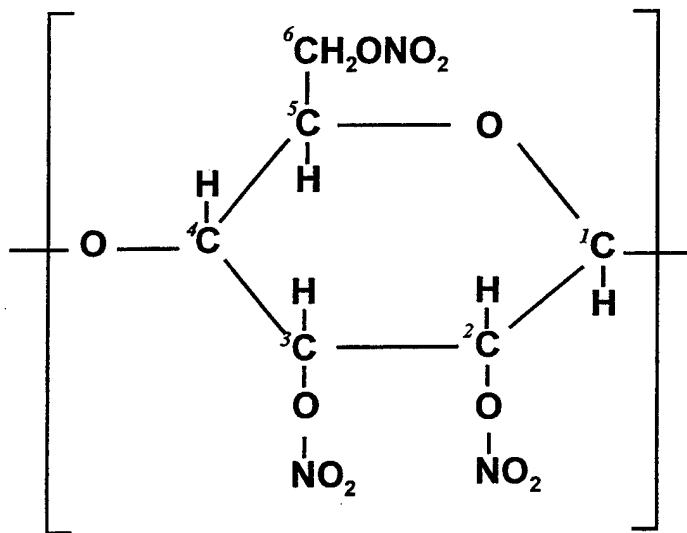


Figure 4. Nitrocellulose monomer unit showing the three possible sites of nitration.

The degree of nitration of a given specimen of NC is characterized by the percent nitration (%N) or average mass of nitrogen per mass of the specimen. The pure trinitrate homopolymer has a %N of 14.1, the pure dinitrate homopolymer 11.1%,

and the pure mononitrate homopolymer 6.8%. Military grades of NC typically have an average %N in the range of 12–13%, and Leider and Seaton (1979) found that they are a mixture of all three nitrate states.

We chose to treat NC as a homogeneous mixture of the three nitration states with their distribution computed from a Monte-Carlo code we developed based on the findings of Leider and Seaton (1979). They found that the C6 site is always nitrated first, and then either the C2 and C3 sites are next with equal probability. The C6 site primacy is confirmed by the N15 tagged decomposition experiments of Gelernter et al. (1956). We confirmed the assumption of equal probability of C2 and C3 site nitration by independent calculations of NO₂ binding energies at either site. *Ab initio* calculations (Bunte and Miller unpublished results) established the binding energies to differ by about 1 kcal/mole, and the calculations are not expected to be distinguishable at this level. Similar calculations (Bunte and Miller, unpublished results) put the binding energy of the NO₂ at the C6 site at about 5 kcal greater, consistent with the Gelernter et al. (1956) experimental work. The distribution of nitrate states for various given nitration levels, as computed by our Monte-Carlo code, is given in Figure 5.

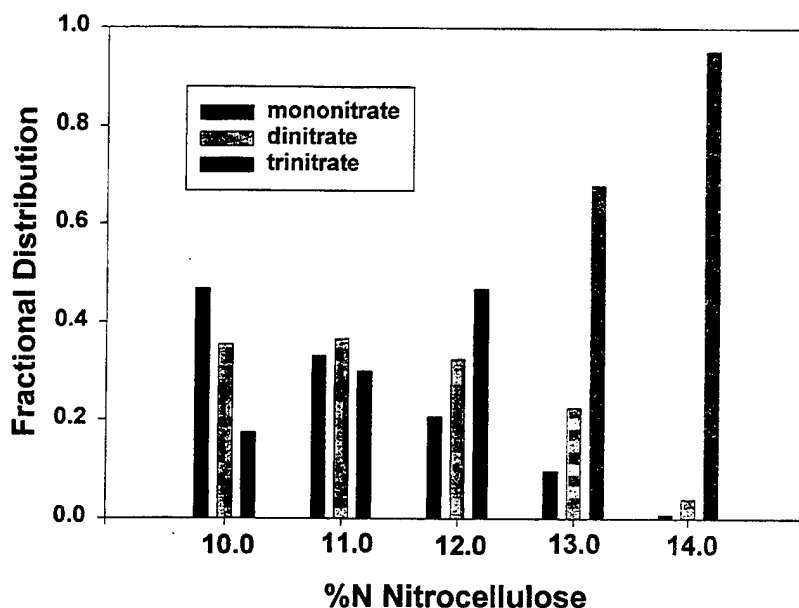


Figure 5. Results of a Monte-Carlo calculation of nitrate-state distribution in nitrocellulose as a function of nitration level.

3.2.2 Propellant Density Predictions

A full molecular simulation was performed on the gun propellant JA2 (strictly speaking a triple-base propellant but often referred to as a double-base propellant). The NC in JA2 has an average %N of 13.1. Using the

aforementioned Monte-Carlo code, the distribution of nitrate states for 13.1% N NC polymer was determined to be 11 tri-, 3 di-, and 1 mononitrate for a polymer chain consisting of 15 monomer units. A heteropolymer with this distribution was constructed, and an MD NPT simulation was run. This simulation resulted in a computed density of 1.6151 g/cm³. To our knowledge, the density of 13.1%N NC has not been measured; however, 12.2%N NC has a density of 1.653 g/cm³, and 13.45% N NC has a density of 1.665 g/cm³. Interpolating between these two known densities results in an estimated density of 1.661 g/cm³. Our computed density is within 3% of this value.

The propellant JA2 consists of roughly 60% (by weight) NC (13.1%N), 25% DEGDN, and 15% NG. Having successfully predicted the density of the individual ingredients, we constructed a cell to simulate JA2. The simulation cell consisted of the usual 10 configurations, each containing 2 strands of NC (13.1%N), 18 molecules of DEGDN, and 9 molecules of NG. Figure 6 shows one such configuration. NPT dynamics were run; the average density of the 10 configurations was 1.595 ± 0.018 g/cm³. The measured density of JA2 is 1.57 ± 0.01 g/cm³ (Miller and Kotlar 1992). Our simulated density differs from the measured density by 1.6%. Figure 6 is a most remarkable image, being the first molecular view of a real propellant formulation ever produced.

In support of a propellant burning-rate predictor model (Miller and Anderson 2000) being developed at the U.S. Army Research Laboratory (ARL), we also ran molecular simulations of the mononitrate homopolymer, dinitrate homopolymer, and trinitrate homopolymer. This burning-rate model treats nitrocellulose as a simple noninteracting mixture of these three homopolymers with mole fractions computed by the Monte-Carlo code described previously; the propellant density is then computed using additive molar volumes of the propellant ingredients. In order to do this, one must know the densities of each of the pure homopolymers, which to our knowledge have not been measured experimentally, and in fact may be impossible to synthesize. Using the COMPASS force field, the computed densities of these three homopolymers are

- mononitrate homopolymer, 1.5250 g/cm³,
- dinitrate homopolymer, 1.5778 g/cm³, and
- trinitrate homopolymer, 1.6640 g/cm³.

We have found that the results obtained using the additive molar volume methodology are generally in excellent agreement with measured propellant densities, and this fact indirectly corroborates the homopolymer densities previously reported. For example, the computed density of M9, a double-base propellant, is 1.621 g/cm³, compared to the measured value of 1.62 ± 0.02 g/cm³ (Miller and Kotlar 1992). In the case of JA2, the density is estimated to be

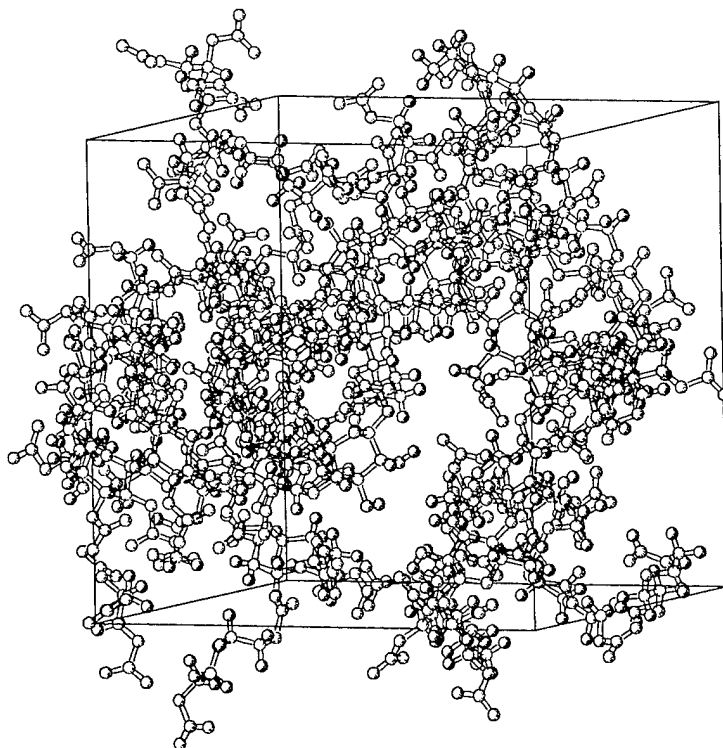


Figure 6. Molecular model of the gun propellant JA2. Red corresponds to oxygen atoms, blue corresponds to nitrogen atoms, black corresponds to carbon atoms, and white corresponds to hydrogen atoms.

1.558 g/cm³ compared with a measured value of 1.57 ± 0.01 g/cm³, an error of 0.8% (Miller and Kotlar 1992). A single-base propellant, M10, gave less accurate results: 1.660 g/cm³ compared with 1.51 ± 0.01 g/cm³ measured (Miller and Kotlar 1992). The single base propellant is poorly plasticised; this less impressive result is likely due to the creation of internal voids in the actual propellant during drying. Such special cases would require an atomistic model which mathematically follows the diffusion of solvent from the molecular interstices.

4. Conclusions

We have used atomistic simulation techniques to predict *a priori* the densities of the following energetic ingredients of the gun propellant JA2: nitrocellulose (NC), diethyleneglycol dinitrate (DEGDN), and nitroglycerin (NG). In addition, we have combined these ingredients in a simulation to predict the density of JA2 within 1.6% of its measured value. These results are the first *a priori* prediction of the density of an actual Army gun propellant and clearly demonstrate the predictive capability of this methodology. This methodology will be a valuable

tool for propellant chemists and formulators to aid in developing new high energy propellants for applications in the Future Combat System. Current efforts are being directed towards parameterizing and validating additional energetic functional groups such as nitramines (-NNO₂) and azides (-N₃) in the COMPASS force field.

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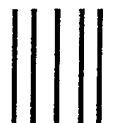
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